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# Electrochemical Determination of Benzene Substituted Derivatives using Carbon Based Purine Electrodes through Electrochemical Impedance Spectroscopy

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Purine nucleobases, guanine and adenine, are known electroactive compounds which get oxidized over the carbon electrodes. These compounds are found to react with benzene derivatives forming its adducts. The formation of these adducts was electrochemically monitored using carbon electrodes from the changes in oxidation signals. Four different forms of carbon namely, Graphite, Activated Carbon, Glassy Carbon and Multi-walled Carbon nanotubes were made into a form of paste and coated over graphite electrode separately. Mixtures of guanine and adenine were prepared and electrostatically bounded over the working electrodes coated with carbon allotropes paste using positive potential difference (+0.3V). 0.1M NaCl containing 10/10mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ was used to study the film forming abilities of the working electrode. Electron transfer resistance was obtained through non-linear regression analysis of the semicircle portion in Nyquist plot. The standardized working electrode was exposed to various concentrations of mono-, di- and poly-substituted benzene derivatives. The anodic current around 0.7 and 1.0V was used as oxidation signal for guanine and adenine respectively. Calibration plot were obtained for benzene substituted derivatives using EIS. The detection limit of benzene was found to be 10 ng/ml for mono-substituted derivatives and 30 ng/ml for di- and poly- substituted benzene derivatives in MWCNT based purine electrodes.

**Keywords:** Benzene Substituted Derivatives, Carbon Based Purine Electrodes, Differential Pulse Voltammetry, Electrochemical Impedance Spectroscopy, Purine nucleobases

## 1. INTRODUCTION

Purine bases, the heterocyclic aromatic compounds with a pyramidine ring fused to imidazole ring are known to react with benzene [1] and its derivatives [2] forming its adducts. These purine bases

are known to get oxidized over carbon electrodes [3]. This property of purine bases have been used in the identification of toxins [4], micro-organisms [5], hybridization [6], electrocatalysis [7] etc. Carbon is a non-metallic chemical containing four valance electrons to form covalent bonds with other compounds. Several allotropes of carbon exist in nature such as graphite, glassy carbon, graphene, diamond, fullerene, carbon nanotubes etc. The chemical, physical, electrical and mechanical properties of these allotropes are known to vary for each compound [8]. In this report, four allotropes namely graphite, activated carbon, glassy carbon and carbon nanotubes were used to study their electrostatic binding capacity with purine bases and further its application in the determination of benzene and its derivatives

The electrical and structural properties of the carbon allotropes play a major role for its application in biosensor. Larger the surface area of the allotropes, greater are the available sites for the sensing materials to bind and greater the electrical conductivity, greater the sensing ability. Graphite, a semimetal, is the most stable and widely used carbon allotrope. The carbon atoms arranged in the planar graphite represent the structure of honey comb lattice (lattice separation: 0.142nm and planar distance: 0.335nm). The delocalization of valance electrons is known to occur within the carbon layers during electrical conductivity [8]. Activated carbon, commonly known as activated charcoal is formed by chemical activation of charcoal by strong acid, base or salt, followed by carbonization or oxidation, resulting in the formation of tiny pores between the carbon atoms. These pores enhance the surface area to volume ratio to 150 to 2000 $m^2/g$ [9]. Glassy carbon (glass like carbon), combines glassy and ceramic properties with those of graphite [10]. Electrochemically, glassy carbon electrode in aqueous solutions is considered to be an inert electrode for hydronium ion reduction [11]. Several studies have been reported for its application as working electrode for purine based biosensors. Multiwalled carbon nanotubes posses' greater surface to volume ratio as its diameter ranges in nanoscale and its length ranges in several microns. Reports on the MWCNT modified electrodes suggest its application in biosensors for its effective immobilization of the electroactive materials and electrical conductivity [12].

One of the major problems associated with carbon based biosensor is the low solubility of carbon based compounds in usual solvents. Dispersion of carbon allotropes in the solvent followed by immobilization of the sensing material is an interesting approach to prepare electrochemical sensors [13]. The resulting modified electrodes have been employed for the detection of various bioanalytes including glucose, antibodies, virus, bacterial DNA etc [14]. This paper makes an electrochemical comparison of the electrostatic binding ability of the purine bases over the above mentioned four carbon allotropes for the formation of stable biorecognition layer for the electrochemical detection of benzene substituted derivatives. Special focus was given for the experimental condition on the concentrations of carbon allotropes and immobilization concentration since these two parameters form a major role in the detection limit of the analytes. The interaction of analytes with the biosensor was evaluated from the change in electrochemical response before and after its interaction using electrochemical impedance spectroscopy.

## 2. EXPERIMENTAL

### *2.1. Reagents and Solution*

Guanine and adenine were purchased from Sisco Research Laboratories, Maharashtra, India. Graphite rods were purchased from HomeScience Tools, Montana, USA. The procured rods were cut into 5 equal sizes and rubbed over micro alumina powder for several minutes until a smooth surface of diameter 0.636 cm was obtained. In order to enable the electrical contact, conducting wires of equal length were pasted at the side of the sliced graphite rods using silver paste. It was then coated with Teflon leaving the bottom surface for it to act as sensor after modifications. Graphite powder, activated carbon and glassy carbon were purchased from Alfa Aeser, Hydrabad, India. MWCNTs were obtained from Applied Science Innovations PVT. Ltd, Maharastra, India. All the four compounds were oxidized using concentrated nitric acid by sonicating it for 30 minutes, in order to remove the impurities. Double distilled water was used throughout the experiment. All the other chemicals were procured from Sisco Research Laborotaries and were used without any further purification.

DPV measurements were carried in 0.1M phosphate buffer at pH 7. CV and EIS measurements were carried out in 0.1M NaCl solution containing 10/10mM $K_3Fe(CN)_6/K_4Fe(CN)_6$. Stock solutions of guanine and adenine were prepared by dissolving its appropriate amount in 0.1M HCl and later diluting it with water. Solutions of benzene substituted derivatives were prepared immediately before each experiment.

### *2.2. Apparatus*

All the electrochemical measurements were recorded using the instrument SP-300 from Biologic Science Instrument, France, running on EC-Lab Software (Version 10.18) and with standard calomel electrode as reference electrode, platinum wire as counter electrode and graphite electrode (surface area = 0.318 $cm^2$) as working electrode. All the electrochemical experiments were conducted in a 20ml cell containing 15ml of the supporting electrolyte.

### *2.3. Preparation of Modified Electrodes*

Prior to surface modification, graphite electrode was cleaned by polishing with 0.05µm alumina cloth for 1 minute and sonicated in water for 30s. Graphite, activated carbon, glassy carbon and multi-walled carbon nanotubes were sonicated with concentrated nitric acid for 30 minutes. The modified electrode was prepared by casting desired quantity of carbon allotropes' paste graphite (G), activated carbon (AC), glassy garbon (GC) and multi-walled carbon nanotubes (MWCNT) over graphite electrode. It was allowed for drying at room temperature. The resulting electrodes were named as G/G, AC/G, GC/G and MWCNT/G. These electrodes can be reused by rubbing it over 0.05µm alumina cloth until a smooth polished surface is obtained.

*2.4. Immobilization of Purine Bases*

The electrode surface was pretreated by applying a potential of +1.5V for 30s in 0.1M phosphate buffer (pH 5) to remove electrochemical impurities. Purine based biosensor was developed by immobilizing purine nucleobases at a fixed potential (+0.3V versus calomel/platinum electrode for 180s). During immobilization step, the electrode was immersed in 0.1M Phosphate buffer (pH 7) containing desired quantity of guanine and adenine. After immobilization, the electrode was washed with distilled water to remove the unbound purines.

*2.5. Voltammetric Measurements*

The electrochemical properties of modified electrode were studied by cyclic voltammetry (potential from 0 to +1.5V at scan rate of 50mV/s) in 0.1M phosphate buffer solution. 10/10mM solution of $K_3Fe(CN)_6/K_4Fe(CN)_6$ was used as redox probe to study the interface properties of the electrode immobilized with purine bases. 0.1M phosphate buffer solution (pH 7) was used as a supporting electrolyte. Electrochemical impedance measurements were performed at open circuit potentials in 10mM $K_4Fe(CN)_6$ + $K_3Fe(CN)_6$ +0.1M NaCl (pH 7) solutions. The electron transfer resistance was obtained through the non-linear regression analysis of the semicircle portion of the Nyquist plot (Zim vs. Zre). Three replicate measurements were carried out for each experiment to maintain concordance.

*2.6. Electrochemical Determination of Aromatic compounds*

EIS of the purine bases immobilized over modified electrodes were obtained by following the procedure as described above. Then the electrode was immersed in the solution containing various aromatic compounds for 5 minutes for the purine bases in the electrode to react with aromatic compounds. EIS measurements before and after the interaction with aromatic compounds were carried out. The percentage of survived purine nucleobases after aromatic compound interaction was calculated from the change of signals obtained at electrode with and without purine bases related to the difference of signals corresponding to original purine bases as follows:

$$\Delta R_{ct(rel)}\% = [(R_{ct(surv\ PN)} - R_{ct(MWCNT)})/(R_{ct(PN)} - R_{ct(MWCNT)})\ ]* 100 \qquad [1]$$

where $R_{ct}$ is the electron transfer resistance at EIS measured at the peak potential obtained for 10/10mM $K_3Fe(CN)_6/K_4Fe(CN)_6$ in 0.1M NaCl solutions at the modified electrodes without purine bases. The indexes used, characterize the chemical modifiers of graphite electrode.

## 3. RESULTS AND DISCUSSION

Various purine based biosensors with layers of purine nucleosides immobilized over carbon allotropes' interphase at graphite electrode surface have been investigated. Amount and concentration of carbon allotropes were optimized for the maximum immobilization concentration of purine

nucleosides using DPV in 0.1M phosphate buffer solution (pH 7). Electrochemical pretreatment was performed by anodization at 1.5V for 30s (versus standard calomel/platinum reference electrode) in order to electrochemically activate the working electrode and to remove electrochemical impurities at the electrode surface. However the responses of the electrochemically activated working electrode depend on the experimental parameters such as the potential limits, redox reaction time, composition, concentration and pH of the supporting electrolyte. This pretreatment procedure was found to improve the hydrophilic character of the electrode surface [15].

### *3.1. Optimization of Carbon Based Purine Electrodes*

Each of the four carbon allotropes showed different immobilization profile on DPV. The increase in the quantity of carbon allotropes provided more surface area for the DNA to be immobilized over the electrode surface which enhances direct electrochemical response of purine bases [16, 17 and 18]. Hence it is necessary to optimize the minimum quantity of carbon allotropes required to immobilize the known maximal concentration of guanine and adenine for a particular electrode surface area. Figure 1 displays the DPV response of optimized carbon allotropes for purine nucleobases immobilization. It could be noted that optimization was reached at the purine concentrations of 20, 30, 40 and 60mg/l for 3mg/ml graphite, 2.5mg/ml of activated carbon, 2mg/ml of glassy carbon and 1.25mg/ml MWCNT respectively.

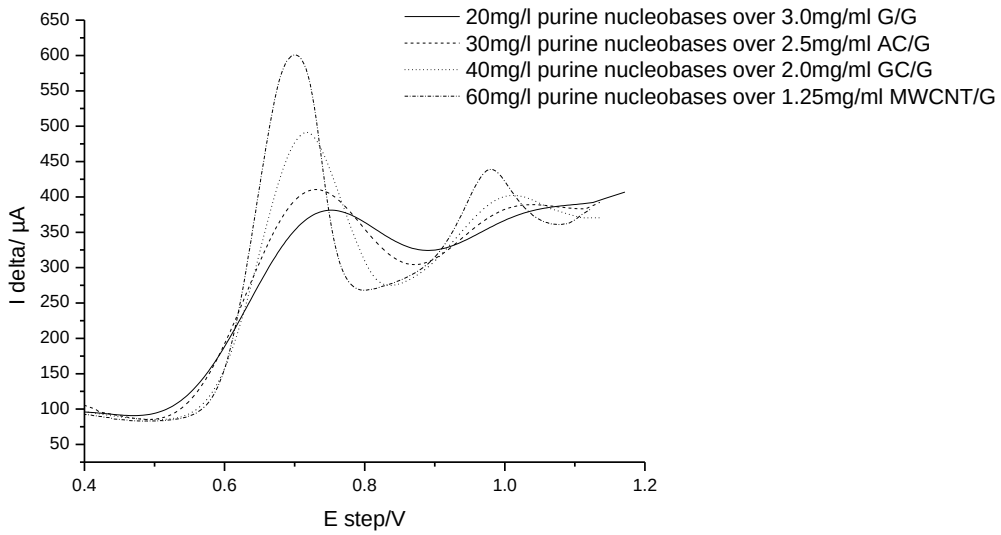


**Figure 1.** DPV response of the optimized carbon based electrode

MWCNT was found to immobilize large amount of purine mixtures at lesser concentration. This is due to its greater surface area compared to other carbon forms, facilitating greater immobilization sites [12]. Secondly, the maximum purine bases immobilized over the modified electrodes decreases even though the concentration of graphite, AC and GC required to obtain

maximum peak was increased. From Figure 1, based on the active immobilization sites, the four forms of carbon can be arranged in increasing order as G<AC<GC<MWCNT. Similarly, greater conductivity of MWCNT is reflected in the maximum peak potential from the DPV response. The peak potentials for G/G, AC/G and GC/G electrodes were shifted to more positive direction compared to MWCNT. This indicates certain degree of resistance exhibited by other three forms of carbon in comparison with MWCNT. The electrical conductivity of the four carbon allotropes can be arranged in the increasing order as G<AC<GC<MWCNT from the obtained DPV response.

### *3.2. Electron transfer characteristics of Carbon Based Purine Electrodes*

In order to study the interfacial electron transfer properties of the carbon based purine electrodes, EIS and CV were performed using the electroactive ferrocyanide/ferricyanide redox couple in 0.1M NaCl solution. Nyquist plot (Figure 2) of the working electrodes displays a semicircle at high frequencies and it is linear at low frequencies. The semicircle portion and the linear portion of the Nyquist plot represent electron transfer- limited process and diffusion limited process respectively [19]. Nyquist plot (dependence of an imaginary part of impedance Z" vs real part of the impedance Z') of the modified electrodes represents a semicircle at high frequencies illustrating an electron transfer limiting process and a short linear part at low frequencies representing the diffusion limiting step of the electrochemical process [19].

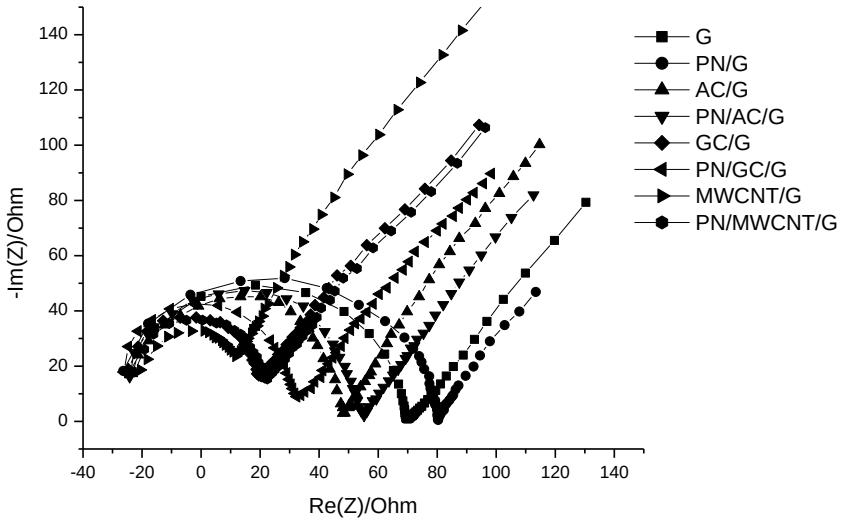


**Figure 2.** Nyquist plot of Carbon based working electrodes in 0.1M NaCl containing 10/10mM $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ ions

For graphite, the semicircle portion is high illustrating increased resistance offered by graphite to the solution for redox charge transfer. Short linear portion at low frequencies illustrates the diffusion limited process and for graphite it could be noticed that the linear portion is short when compared to other three forms of carbon. This indicates very small portion of the charge being diffused into the

electrode coated with graphite paste. On the other hand, MWCNT seems to posses least resistance and greater diffusion illustrated from the small semicircle and long linear portions. From Nyquist plot, it was observed that the charge transfer resistance increases gradually as the surface area of the carbon allotropes increases as G<AC<GC<MWCNT.

It was found that the $R_{sol}$ shows a negative resistance in the Nyquist plot. Numerous examples of negative resistance have been reported and in all the cases, the condition, $Re_{[Z\omega]}$, $\omega \rightarrow 0<0$, is associated with a passivation event in which the steady state current decreases with increasing voltage[20]. In other words, the electrochemical adsorption of a blockage intermediate from the electrolyte over the working electrode is a passive event ultimately represented as a negative resistance. However, the charge transfer resistance is at the positive portion representing the active transport of the redox ions.

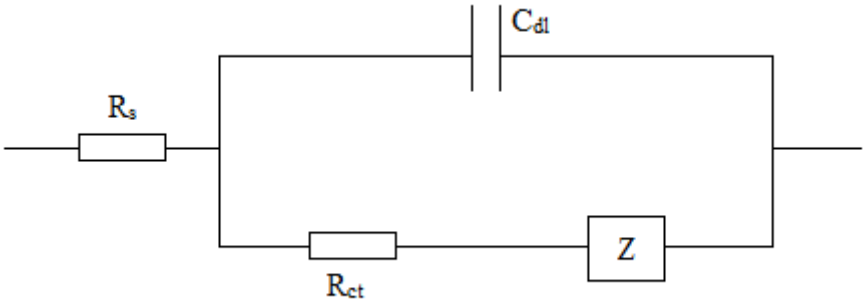


**Figure 3.** The scheme of equivalent circuit simulating the impedance spectra. $R_{sol}$- resistance of the supporting electrolyte, $R_{ct}$- charge transfer resistance, $C_{dl}$-capacitance

**Table 1.** Parameters of the equivalent circuit simulating the complex impedance spectra of the electrodes in the presence of 0.1M NaCl solution containing 10/10mM $K_3Fe(CN)_6/K_4Fe(CN)_6$. $R_{sol}$- resistance of the supporting electrolyte, $R_{ct}$- charge transfer resistance, $C_{dl}$-capacitance.

| Working Electrode | $R_{sol}$, Ω | $R_{ct}$, Ω | $C_{dl}$, μF |
|---|---|---|---|
| G/G | -24.53 | 70.38 | 0.77 |
| PN/G | -26.35 | 80.24 | 0.33 |
| AC/G | -23.24 | 48.90 | 0.95 |
| PN/AC/G | -24.16 | 55.24 | 0.99 |
| GC/G | -24.64 | 20.16 | 80.9 |
| PN/GC/G | -26.38 | 32.51 | 26.4 |
| MWCNT/G | -20.01 | 13.39 | 1873.6 |
| PN/MWCNT/G | -22.30 | 21.60 | 277.2 |

The impedance data were simulated using the Randles equivalent circuit (Figure 3) consisting of a parallel combination of the capacitance ($C_{dl}$) and the charge transfer resistance ($R_{ct}$) and impedance by redox reactions in series with the supporting electrolyte resistance ($R_{sol}$). The fitting of spectras to the equivalent circuit has indicated a good agreement between the circuit model and the real

experimental data, especially at high frequency values. The parameters obtained from the fitting analysis are presented in Table 1. The impedance plots of the individual electrodes show a significant difference in impedance values reflecting its electrode surface properties. The presence of the carbon allotropes significantly decreases the impedance (G>AC>GC>MWCNT). It can be illustrated that the presence of MWCNT gives a least impedance value due to its high conductivity.

The increase or decrease in $R_{ct}$ reflecting the increase or decrease in the diameter of the semicircle is directly associated with the blockage behavior of the electrode surface for the charge transfer to the redox couple in the supporting electrolyte [21]. For bare graphite, the value of $R_{ct}$ is 70.38 Ω and it reflects the semicircle part with greater diameter. As the purine bases are introduced to the graphite surface, the diameter of the semicircle increases (80.24Ω) due to the increase in the charge transfer resistance formed by the purine nucleobases film over the G/G electrode. The diameter of the semicircle decreases, with the presence of AC (48.90Ω), GC (20.16Ω) and MWCNT (13.39Ω) seperately. MWCNT/G electrode possesses least resistance in the impedance spectra and hence MWCNT immobilized on the graphite surface plays an important role similar to an electron conducting tunnel making electron transfer to the electrode surface easier. In all the cases, the nucleobases immobilized Nyquist plot shows a greater resistance in comparison with its subsequent carbon allotrophes modified electrode. The increase in the $R_{ct}$ value for electrode containing purine nucleobases is due to the formation of highly organized layer of the purine bases over the modified electrode, resulting in the blockage of electron transfer to the redox couple, in other words, restricting the redox species to penetrate the carbon allotrophes' layer [22].

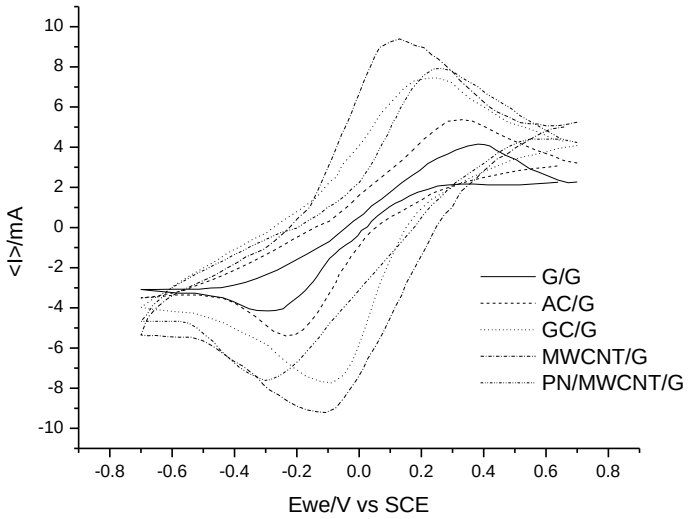


**Figure 4.** CV of modified electrode in 1M NaCl containing 10/10mM $K_4Fe(CN)_6/K_3Fe(CN)_6$ at pH 7.

To confirm EIS, CV was performed in the same supporting electrolyte. The mechanism of purine detection using $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ resides in the barrier effect of the negatively charged purine bases towards the redox couple. This results in the reduction in redox couple signal evaluated against the base line [23]. Figure 4 displays the CV of the various modified graphite electrodes in

$K_4Fe(CN)_6/K_3Fe(CN)_6$ redox couple. The coating of carbon allotropes significantly improves the electrochemical reversibility of the redox probe and at the same time increases its current response. The addition of purine layer leads to increase in ΔEp (anodic to cathodic peak potential difference) and a decrease in the cathodic current. ΔEp, the peak potential difference between the redox peak is theoretically 59mV and in practice, the difference is typically 70 to 100 mV. At the same time, non-symmetric redox peaks are the indications of irreversible reaction [24]. In all the modified electrodes, ΔEp was found to between 200 to 700 mV which is beyond the characteristic peak potential difference for reversible reaction. However, the anodic to cathodic peak current ratio is symmetric and in the range of 0.89 - 1.01, confirming the reversibility of the redox couple [25]. In the presence of purine nucleobases, ΔEp increases and the cathodic peak current decreases, increasing the Ia/Ic ratio to 1.04. Table 2 summarises the peak potential separation (ΔEp) and anodic to cathodic peak current ratio (Ia/Ic) obtained for various modified electrodes.

**Table 2.** CV parameters of modified electrode in 10mM $K_4Fe(CN)_6$ + $K_3Fe(CN)_6$ +0.1M NaCl (pH 7) electrolyte.

| | ΔEp, v | Ia/Ic |
|---|---|---|
| G/G | 0.682 | 0.99 |
| AC/G | 0.537 | 0.99 |
| GC/G | 0.324 | 0.96 |
| MWCNT/G | 0.236 | 1.01 |
| PN/MWCNT/G | 0.571 | 1.04 |

*3.3. Electrochemical Determination of Benzene and its substituted derivatives*

Purine bases were attacked by exposing the PN/MWCNTG electrode to benzene substituted derivatives. Biosensors of equivalent mixtures of guanine and adenine were prepared at a concentration of 60 mg/l and were placed in contact with the analytes. Survived purine bases were calculated from the change in the charge transfer resistance values before and after the exposure. Figure 5 displays the calibration curves obtained from the relative portion of survived purine nucleobases from EIS spectra. The detection limit was found to be 10ng/l for mono substituted derivatives and 30ng/l for di- and poly substituted benzene derivatives. It could be noted that beyond certain concentrations of benzene derivatives, the survived purine response almost remained stable representing the saturation level. The challenge in the making of biosensor lies in increasing this saturation level. This could happen if large quantity of purine bases were available for the analyte to react with. For the derivatives of benzene, the detection limit and the saturation level varies depending on the analyte's reaction with the sensing material. However, a nearly linear behavior was observed for most of its derivatives in the approximate concentration range 40 to 80 ng/ml for mono-substituted derivatives, 50 to 80ng/ml for di-substituted derivatives and 20 to 80 ng/ml for poly-substituted derivatives. Fitting of the linear regression data is most common and simple method used for the

calibration of sensing device [26]. The calibration curve data can be used as a backbone for the detection of these compounds within the specified linear range.

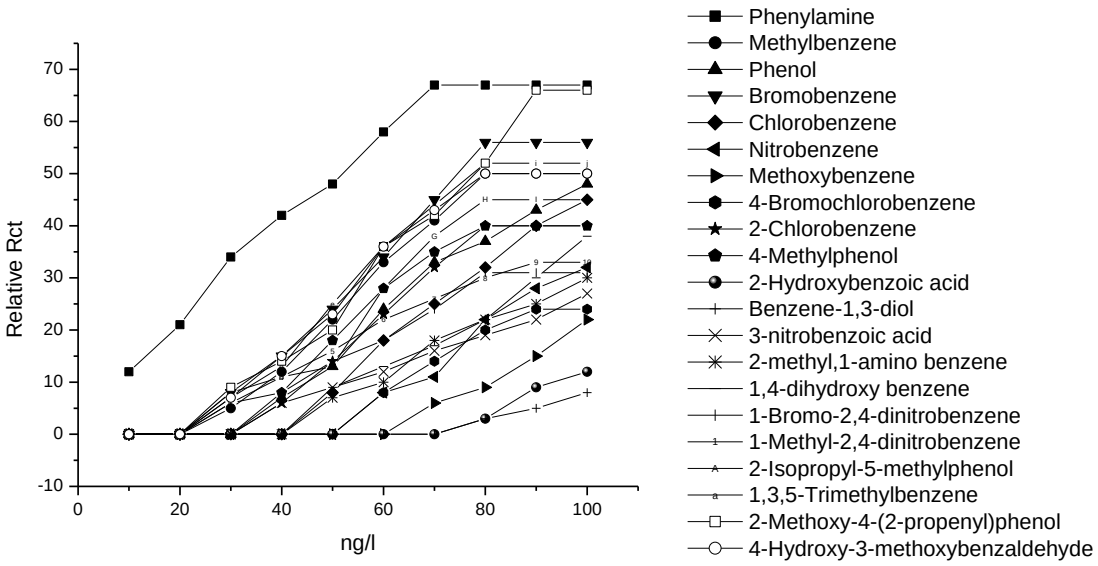


**Figure 5.** Calibration curves for the detection of benzene substituted derivatives by the standardized purine nucleobases immobilized MWCNT modified graphite electrode.

## 4. CONCLUSIONS

The data presented here can be used for the detection of benzene substituted derivatives within the specified linear range. The immobilization of purine nucleobases at the surface of MWCNT coated graphite electrode has a great importance in this study due to its least charge transfer resistance. Both hydrophobic and electrostatic interactions contribute to the adsorption of guanine and adenine on the working electrode surface. DPV has been used to study the oxidation peaks of the nucleobases after immobilization and EIS and CV have been used to study the film forming abilities of the purine nucleobases for the fabrication of biosensor for the detection of benzene substituted derivatives. This biosensor has several advantages including reproducibility and sensitivity. It should be noted that in-vitro reaction conditions are different from the electrochemical reaction conditions.

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